(12) UK Patent Application (19) GB (11) 2 143 542 A

(43) Application published 13 Feb 1985

(21) Application No 8416181

(22) Date of filing 25 Jun 1984

(30) Priority data
(31) 3521/83 (32) 28 Jun 1983 (33) CH

(51) INT CL³
C09B 57/00 B41M 5/12

(52) Domestic classification
C4P 100 D1X
U1S 2250 C4P

(56) Documents cited
GB A 2068994

(58) Field of search
C4P

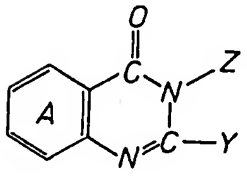
(71) Applicant
Ciba-Geigy AG (Switzerland),
Klybeckstrasse 141, 4002 Basle, Switzerland

(72) Inventors
Rudolf Zink
Ian John Fletcher

(74) Agent and/or Address for Service
T Sharman,
Ciba-Geigy PLC, Tenax Road, Trafford Park,
Manchester M17 1WT

(54) Chromogenic quinazolones

(57) New chromogenic quinazolones are of formula



wherein

Y is a polycyclic non-aromatic heterocyclic radical which is attached to the quinazolone moiety through a fused benzene nucleus and is unsubstituted or substituted, and

Z is hydrogen, alkyl which is unsubstituted or substituted by halogen, hydroxy, cyano or lower alkoxy, or is cycloalkyl, phenyl, benzyl, or phenyl or benzyl which are each substituted by halogen, nitro, cyano, lower alkyl, lower alkoxy or lower alkoxycarbonyl, and

the ring A is unsubstituted or substituted by halogen, cyano, nitro, lower alkyl, lower alkoxy or lower alkoxycarbonyl.

These compounds are particularly suitable colour formers in pressure-sensitive or heat-sensitive recording materials and produce strong greenish yellow colorations of excellent fastness to light and sublimation.

GB 2 143 542 A

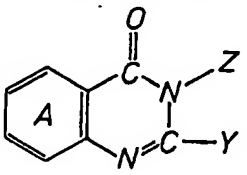
SPECIFICATION

Chromogenic quinazolones

The present invention relates to chromogenic quinazolines, to the preparation thereof, and to the use of these compounds as colour formers in pressure-sensitive or heat-sensitive recording materials.

The novel chromogenic quinazolines have the general formula

(1)



wherein

Y is a polycyclic non-aromatic heterocyclic radical which is attached to the quinazoline moiety through a fused benzene nucleus and is unsubstituted or substituted, and

Z is hydrogen, alkyl which contains not more than 12 carbon atoms and is unsubstituted or substituted by halogen, hydroxy, cyano or lower alkoxy, or is cycloalkyl, phenyl, benzyl, or phenyl or benzyl which are each substituted by halogen, nitro, cyano, lower alkyl, lower alkoxy or lower alkoxycarbonyl, and

the ring A is unsubstituted or substituted by halogen, cyano, nitro, lower alkyl, lower alkoxy or lower alkoxycarbonyl.

In the definition of the radicals of the quinazolones, lower alkyl and lower alkoxy normally denote those groups or moieties which contain 1 to 5, preferably 1 to 3, carbon atoms.

Examples of lower alkyl groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl or amyl; and lower alkoxy groups are for example methoxy, ethoxy or isopropoxy.

Halogen is for example fluorine, bromine or, preferably, chlorine.

Alkyl groups Z may be straight chain or branched. Examples of such alkyl groups are: methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, amyl, n-hexyl, 2-ethyl-hexyl, isooctyl, n-octyl, decyl or n-dodecyl.

Substituted alkyl radicals Z are preferably cyanoalkyl, haloalkyl, hydroxyalkyl or alkoxyalkyl, each containing preferably a total of 2 to 6 carbon atoms, e.g. β-cyanoethyl, β-chloroethyl, γ-chloropropyl, β-hydroxyethyl, γ-hydroxypropyl, β-methoxyethyl or β-ethoxyethyl.

Z as cycloalkyl is for example cyclopentyl or, preferably, cyclohexyl.

Preferred substituents in the benzyl and phenyl moiety of the radicals Z are e.g. halogen, cyano, methyl, methoxy or carbomethoxy. Examples of such araliphatic and aromatic radicals are: methylbenzyl, chlorobenzyl, cyanophenyl, tolyl, xylyl, chlorophenyl, methoxyphenyl or carbomethoxyphenyl.

Z in formula (1) is preferably lower alkyl, benzyl, phenyl or, preferably, hydrogen.

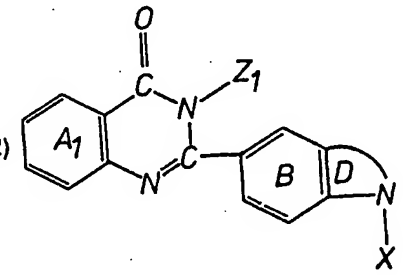
Suitable non-aromatic compounds for the radical Y are e.g. N-unsubstituted or N-substituted indolines, tetrahydrocarbazoles, dihydro- or tetrahydroquinolines, dibenzylimides or benzomorpholines. Y is attached to the quinazolone moiety through the fused benzene ring of the heterocyclic ring systems referred to above. Preferred radicals Y are the indolinyl, dihydroquinolinyl, tetrahydroquinolinyl and benzomorpholino radicals.

The polycyclic heterocyclic compounds for the radical Y can also be ring-substituted by one or more C-substituents. Suitable C-substituents are e.g. halogens, hydroxyl, cyano, lower alkyl, lower alkoxy, lower alkoxycarbonyl, C_1–C_8acyl, preferably lower alkylcarbonyl, alkylene, cycloalkyl, benzyl or phenyl; and N-substituents are e.g. C_1–C_{12}alkyl, C_3–C_{12}alkenyl or benzyl, each of which can also be substituted e.g. by cyano, halogen, hydroxyl, lower alkyl, lower alkoxy or lower alkoxycarbonyl. The alkyl and alkenyl radicals can be straight chain or branched. Examples of alkyl radicals are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, amyl, n-hexyl, 2-ethyl-hexyl, isooctyl, n-octyl, decyl or n-dodecyl; and alkenyl is for example allyl, 2-methallyl, 2-ethallyl, 2-butenyl or octenyl.

Acyl is preferably formyl, lower alkylcarbonyl, e.g. acetyl or propionyl, or benzoyl. Further acyl radicals are lower alkylsulfonyl, e.g. methylsulfonyl or ethylsulfonyl, and phenylsulfonyl. Benzoyl and phenylsulfonyl can be substituted by halogen, methyl, methoxy or ethoxy.

The ring A is preferably not further substituted. If it does contain substituents, then it is preferably mono- or disubstituted by halogen, cyano, lower alkyl or lower alkoxy, e.g. by cyano, chlorine, methyl or methoxy.

Interesting chromogenic quinazolones are those of the formula

(2) 

wherein

X is hydrogen, alkyl which contains not more than 8 carbon atoms and is unsubstituted or substituted by halogen, cyano or lower alkoxy, or is cycloalkyl or benzyl,

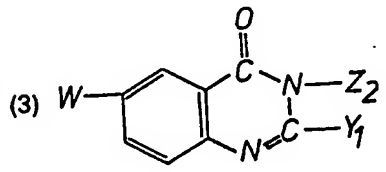
Z_1 is alkyl which contains not more than 8 carbon atoms and is unsubstituted or substituted by lower alkoxy, or is cyclohexyl, phenyl, benzyl, or phenyl or benzyl which are substituted by halogen, cyano, lower alkyl, lower alkoxy or lower alkoxycarbonyl, and the rings

A_1 and B, each independently of the other, are unsubstituted or substituted by cyano, halogen, lower alkyl, e.g. methyl, or lower alkoxy, e.g. methoxy, and the ring

D is a hydrogenated 5- or 6-membered N-heterocyclic ring system which may contain a further hetero atom, e.g. oxygen, sulfur or nitrogen, as ring member, and is unsubstituted or C-substituted by one or—depending on the substituents—more of the same or different substituents selected from halogen, cyano, hydroxyl, lower alkyl, lower alkoxy, C_5–C_6cycloalkyl, benzyl and C_3–C_6-alkylene.

Preferred quinazolones of the formula (2) are those in which Z_1 is lower alkyl, benzyl, phenyl or, most preferably, hydrogen. X is preferably lower alkyl, benzyl or β-cyanoethyl. The ring D is preferably 6-membered and C-substituted in particular by 1, 2 or 3 methyl groups. The rings A_1 and B are preferably unsubstituted. However, the ring B can advantageously contain a methyl group.

Particularly interesting quinazolones are those of the formula

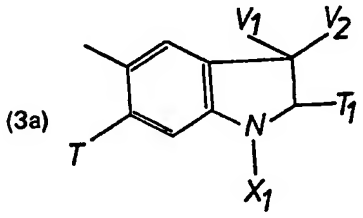
(3) 

wherein

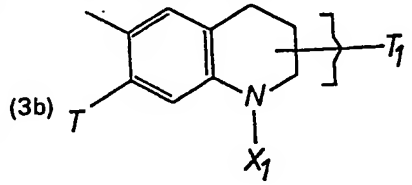
Z_2 is hydrogen, lower alkyl, phenyl or benzyl,

W is halogen, methyl, methoxy or, preferably, hydrogen, and

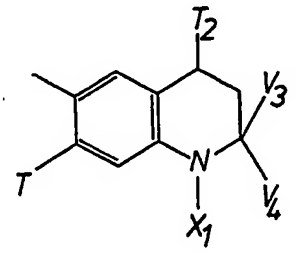
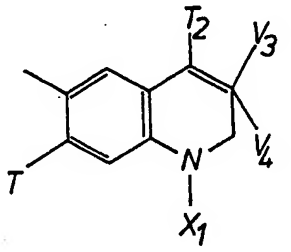
Y_1 is a 5-indolinyl radical of the formula

(3a) 

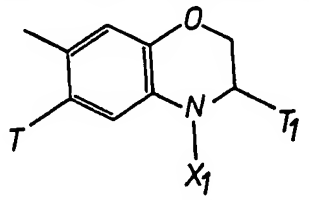
a tetrahydroquinolinyl radical of the formula

(3b) 

a hydrogenated quinoline radical of the formula

(3c)  or  (3d)

or a benzomorpholino radical of the formula

(3e) 

X_1 is hydrogen, C_1–C_8alkyl, C_2–C_6alkoxyalkyl, β-cyanoethyl or benzyl,
T is hydrogen, halogen, lower alkyl, lower alkoxy, C_1–C_4acylamino or phenyl,
T_1 and T_2 are each hydrogen, halogen, hydroxy, lower alkyl or lower alkoxy, and
V_1, V_2, V_3 and V_4 are each hydrogen, lower alkyl, cycloalkyl or benzyl, or (V_1 and V_2) or (V_3 and V_4) are each together alkylene.

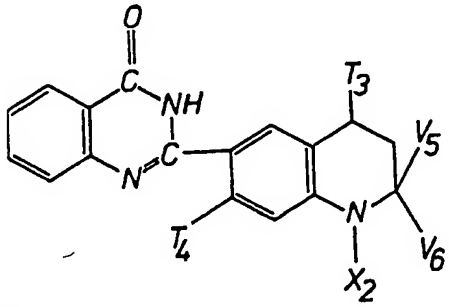
In formula (3), Z_2 is preferably phenyl or, most preferably, hydrogen.

The N-substituent X_1 is preferably benzyl, β-cyanoethyl or C_1–C_8alkyl, e.g. n-octyl, n-butyl, isopropyl or, preferably, methyl or ethyl.

Y_1 is preferably the tetrahydroquinoline radical of the formula (3c). T is preferably hydrogen or methyl. T_1 is preferably hydrogen, methyl, hydroxyl or chlorine. T_2 is preferably hydrogen, methyl or ethyl. V_1 and V_2 are preferably hydrogen or methyl. V_3 and V_4 are preferably each lower alkyl and most preferably are each methyl.

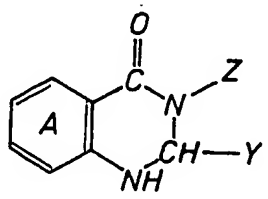
If (V_1 and V_2) or (V_3 and V_4) together are alkylene, then they contain preferably 4 or 5 carbon atoms and, together with the carbon atom to which they are attached, form a cyclopentane or cyclohexane ring. W is preferably hydrogen, halogen or lower alkoxy, e.g. chlorine or methoxy.

Particularly preferred quinazolones are those of the formula

(4) 

wherein
X_2 is C_1–C_8alkyl, β-cyanoethyl or benzyl,
T_3, V_5 and V_6 are each lower alkyl, preferably methyl or ethyl, and T_4 is hydrogen or methyl.

The quinazolones of the formula (1) are prepared by oxidising a 1,2,3,4-tetrahydroquinazol-4-one of the formula

(5) 

wherein A, Z and Y have the given meanings.

The oxidation of the 1,2,3,4-tetrahydroquinazol-4-ones of the formula (5) to give the quinazolones of the formula (1) is carried out with oxidising agents. Suitable oxidising agents are e.g. chromates, bichromates, chlorates, chlorites, peroxides, e.g. hydrogen peroxide, manganese dioxide, lead dioxide, molecular oxygen, air, perborates, permanganates, nitrites, chlorine, bromine and, in particular, chloranil or bisulfites.

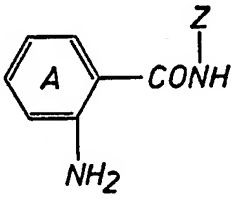
It is advantageous to carry out the reaction in the presence of an organic solvent which does not participate in the oxidation.

Examples of suitable solvents are lower aliphatic alcohols such as methanol, ethanol or isopropanol; alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl or monoethyl ether; or cyclic ethers such as dioxan or tetrahydrofuran; and dimethylformamide, dimethylsulfoxide or acetonitrile.

The best results with respect to yield and purity of the 4-quinazolones are obtained with chloranil as preferred oxidising agent. The oxidation with sodium bisulfite affords ecological advantages. Following the procedure described in Synthesis 1981, (1), 35, quinazolones of the formula (1) are obtained in good yield and purity using this oxidising agent.

The oxidation temperature depends as a rule on the oxidising agent and also on the boiling point of the solvent employed. It is conveniently in the range from 20° to 150°C, preferably from 20° to 100°C. When using chloranil or sodium bisulfite the oxidation is carried out preferably in the temperature range from 20° to 70°C.

The starting materials of the formula (5) can be prepared by reacting e.g. a 2-aminobenzamide of the formula



(6)

with an aldehyde of the formula

Y–CHO (7)

This reaction is conveniently carried out in an organic solvent and at reflux temperature. Suitable solvents are again lower aliphatic alcohols such as ethanol, isopropanol, ethylene glycol monomethyl or monoethyl ether; or aromatic hydrocarbons such as benzene, toluene or xylene.

The quinazolones of the formula (1) to (4) are normally colourless or, at most, faintly coloured. When these colour formers are brought into contact preferably with an acid developer, e.g. an electron acceptor, they produce—depending on the meaning of Z and, in particular, Y—strong yellow or orange shades of excellent fastness to sublimation and light. They are therefore also very useful when combined with one or more other known colour formers, for example 3,3-(bis-aminophenyl)phthalides, 3,3-(bis-indolyl)phthalides, 3-aminophenyl-3-indolylazaphthalides, 3-aminofluoranes, 2,6-diaminofluoranes, leucoauramines, spiropyranes, spirodipyranes, chromeno-indoles, chromenopyrazoles, phenoxazines, phenothiazines, 2-aminophenyl-quinazolines, bisquinazolines, carbazolylmethanes or other triarylmethaneleuco dyes, to give blue, navy blue, grey or black colorations.

The quinazolones of the formulae (1) to (4) exhibit both on phenolic substrates, and especially on clays, an excellent colour intensity and lightfastness. They are suitable in particular as rapidly developing colour formers for use in a heat-sensitive, or especially in a pressure-sensitive, recording material which can also be a copying material. They are distinguished by the property that they have excellent solubility in the capsule oils and exhibit only insignificant loss of colour intensity (CB decline) on exposure in a CB sheet.

A pressure-sensitive material consists, for example, of at least one pair of sheets which contain at least one colour former of the formula (1) to (4) dissolved in an organic solvent, and a solid electron acceptor as developer.

Typical examples of such developers are activated clays such as attapulgite, acid clay, bentonite, montmorillonite, activated clay, e.g. acid-activated bentonite or montmorillonite, and also zeolith, halloysite, silica, alumina, aluminium sulfate, aluminium phosphate, zinc chloride, zinc nitrate, activated kaolin or any clay, or acidic organic compounds, for example unsubstituted or ring-substituted phenols, salicylic acid or salicylates and their metal salts, or an acidic polymer, for example a phenolic polymer, an alkylphenol acetylene resin, a maleic acid/rosin resin or a partially or completely hydrolysed polymer of maleic acid and styrene, ethylene or vinyl methyl ether, or carboxypolymethylene. Mixtures of these polymers can also be used.

Particulary preferred developers are acid-activated bentonite, zinc salicylates, or the condensa-

tion products of p-substituted phenols with formaldehyde. These last mentioned compounds may also contain zinc.

The developers may also be used in admixture with other basically inert or almost inert pigments or with other auxiliaries such as silica gel or UV absorbers, e.g. 2-(2-hydroxyphenyl)-benzotriazoles. Examples of such pigments are: talcum, titanium dioxide, zinc oxide, chalk, clays such as kaolin, as well as organic pigments, e.g. urea/formaldehyde condensates (BET surface urea: 2–75 m^2/g) or melamine/formaldehyde condensates.

The colour former effects a coloured marking at those points where it comes into contact with the electron acceptor. In order to prevent the colour formers contained in the pressure-sensitive recording material from becoming active prematurely, they are usually separated from the electron acceptor. This separation can conveniently be accomplished by incorporating the colour formers in foamlike, spongelike or honeycomb-like structures. The colour formers are preferably encapsulated in microcapsules, which can normally be ruptured by pressure.

When the capsules are ruptured by pressure, for example with a pencil, the colour former solution is transferred to an adjacent sheet which is coated with an electron acceptor and a coloured area is thus produced. This colour results from the dye which is formed and which is absorbed in the visible range of the electromagnetic spectrum.

The colour formers are encapsulated in the form of solutions in organic solvents. Examples of suitable solvents are preferably non-volatile solvents, for example a polyhalogenated paraffin such as chloroparaffin, or a polyhalogenated diphenyl, such as monochlorodiphenyl or trichlorodiphenyl, and also tricresyl phosphate, di-n-butyl phthalate, dioctyl phthalate, trichlorobenzene, trichloroethylphosphate, an aromatic ether such as benzylphenyl ether, a hydrocarbon oil such as paraffin or kerosene, an alkylated (e.g. with isopropyl, isobutyl, sec- or tert-butyl) derivative of diphenyl, diphenylalkane, naphthalene or terphenyl; dibenzyl toluene, terphenyl, partially hydrogenated terphenyl, a benzylated xylene, or other chlorinated or hydrogenated, condensed aromatic hydrocarbons. Mixtures of different solvents, especially mixtures of paraffin oils or kerosene and diisopropylnaphthalene or partially hydrogenated terphenyl, are often used in order to obtain an optimum solubility for the colour formation, a rapid and intense coloration, and a viscosity which is advantageous for the microencapsulation.

The capsules walls can be formed evenly around the droplets of the colour former solution by coacervation; and the encapsulating material can consist of gelatin and gum arabic, as described e.g. in US patent 2 800 457. The capsules can also be formed preferably from an aminoplast or a modified aminoplast by polycondensation, as described in British patent specifications 989 264, 1 156 725, 1 301 052 and 1 355 124. Also suitable are microcapsules which are formed by interfacial polymerisation, e.g. capsules formed from polyester, polycarbonate, polysulfonamide, polysulfonate, but in particular from polyamide or polyurethane.

The microcapsules containing the colour formers of the formulae (1) to (4) can be used for the production of a wide variety of known kinds of pressure-sensitive copying material. The various systems differ substantially from one another in the arrangement of the capsule, of the colour reactants, and of the support. A preferred arrangement is that in which the encapsulated colour former is in the form of a layer on the back of a transfer sheet and the developer is in the form of a layer on the face of a receiver sheet.

Another arrangement of the components is that wherein the microcapsules which contain the colour former, and the developer, are in or on the same sheet, in the form of one or more individual layers, or are present in the paper pulp.

The capsules are preferably secured to the support by means of a suitable adhesive. As paper is the preferred support, these adhesives are principally paper-coating agents, for example gum arabic, polyvinyl alcohol, hydroxymethylcellulose, casein, methyl cellulose, dextrin, starch or starch derivatives or polymer latices. These latter are e.g. butadiene/styrene copolymers or acrylic homopolymers or copolymers.

The paper employed comprises not only normal paper made from cellulose fibres, but also paper in which the cellulose fibres are replaced (partially or completely) by synthetic polymers.

The compounds of the formulae (1) to (4) can also be employed as colour formers in a thermoreactive recording material. This recording material usually contains at least one carrier, one colour former, one electron acceptor, and optionally also a binder, and/or wax.

Thermoreactive recording systems comprise, for example, heat-sensitive recording or copying materials or papers. These systems are used e.g. for recording information, for example in electronic computers, teleprinters or telewriters, or in recording and measuring instruments, e.g. electrocardiographs. The image (mark) information can also be effected manually with a heated pen. Laser beams can also be used to produce heat-induced marks.

The thermoreactive recording mateial can be composed such that the colour former is dispersed or dissolved in one binder layer and the developer is dissolved or dispersed in the binder in a second layer.

Another possibility comprises in dispersing both the colour former and the developer in one layer. By means of heat the binder is softened at specific areas and the colour former comes into

contact with the developer (electron acceptor) at those points where heat is applied and the desired colour develops at once.

Suitable developers are the same electron acceptors as are used in pressure-senstive papers. Examples of developers are the clays already mentioned and especially phenolic resins, or also the phenolic compounds described e.g. in German Offenlegungsschrift 1 251 348, for example 4-tert-butylphenol, 4-phenylphenol, methylene bis-(2-methylphenyol), 4-hydroxydiphenyl ether, α-naphthol, β-naphthol, methyl 4-hydroxybenzoate, 4-hydroxyacetophenone, 2,2'-dihydroxydiphenyl, 4,4'-isopropylidenediphenol, 4,4'-isopropylidene-bis-(2-methylphenol), 4,4'-bis-(hydroxyphenyl) valeric acid, hydroquinone, pyrogallol, phloroglucinol, p-, m- and o-hydroxybenzoic acid, gallic acid, 1-hydroxy-2-naphthoic acid, as well as boric acid or organic, preferably aliphatic, dicarboxylic acids, for example tartaric acid, oxalic acid, maleic acid, citric acid, citraconic acid or succinic acid.

Fusible, film-forming binders are preferably used for the manufacture of the thermoreactive recording material. These binders are normally water-soluble, whereas the quinazolones and the developer are sparingly soluble or insoluble in water. The binder should be able to disperse and fix the colour former and the developer at room temperature.

By applying heat the binder softens or melts, so that the colour former in contact with the developer and a colour is able to form. Examples of binders which are soluble, or at least swellable, in water are e.g. hydrophilic polymers, for example polyvinyl alcohol, polyacrylic acid, hydroxyethylcellulose, methyl cellulose, carboxmethylcellulose, polyacrylamide, polyvinyl pyrrolidone, gelatin, starch, or etherified corn starch.

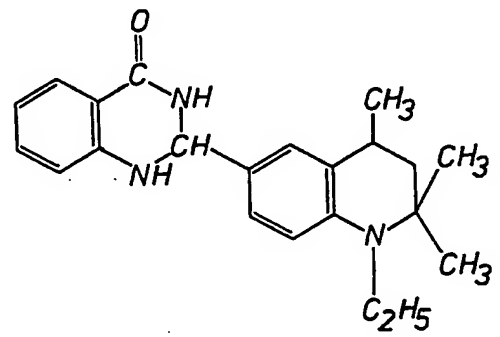
If the colour former and the developer are in two separate layers, it is possible to use water-insoluble binders, i.e. binders which are soluble in non-polar or only weakly polar solvents, for example natural rubber, synthetic rubber, chlorinated rubber, alkyd resins, polystyrene, styrene/butadiene copolymers, polymethylacrylates, ethyl cellulose, nitrocellulose or polyvinyl carbazole. The preferred arrangement, however, is that in which the colour former and the developer are contained in one layer in a water-soluble binder.

The thermoreactive coatings may contain further ingredients. To improve the degree of whiteness, to facilitate the printing of papers, and to prevent the heated pen from sticking, the coatings may contain e.g. talcum, titanium dioxide, zinc oxide, aluminium hydroxide, calcium carbonate (e.g. chalk), clays or also organic pigments, for example urea/formaldehyde polymers. In order to effect the colour formation only within a limited temperature range, it is possible to add substances such as urea, thiourea, diphenyl thiourea, acetamide, acetanilide, stearyl amide, phthalic anhydride, metal stearates, dimethyl terephthalate, phthalonitrile or other appropriate fusible products which induce the simultaneous melting of the colour former and the developer. Thermographic recording materials preferably contain waxes, e.g. carnauba wax, montan wax, paraffin wax, polyethylene wax, condensates of higher fatty acid amides and formaldehyde, or condensates of higher fatty acids and ethylenediamine.

The invention is illustrated by the following Examples, in which percentages are by weight, unless otherwise indicated.

Example 1

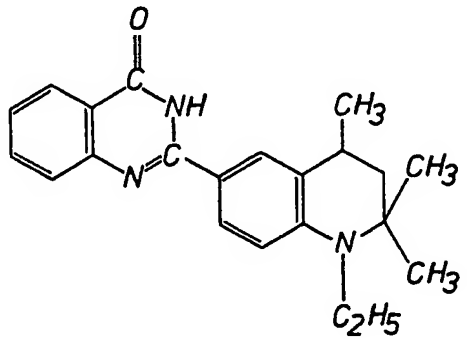
23.1 g of N-ethyl-2,2,4-trimethyltetrahydroquinoline-6-aldehyde are dissolved in 150 ml of ethanol. To this solution are added 13.6 g of anthranilide and 4 ml of 10% sulfuric acid and the reaction mixture is heated to 60°C. The mixture is kept for 1 hour at 60°C and the resultant compound of the formula



(20)

is oxidised by the dropwise addition of a 40% aqueous solution of sodium bisulfite and subsequently stirring the reaction mixture for 2 hours at reflux temperature. After cooling the mixture to room temperature, the precipitate is isolated by filtration, washed with ethanol and dried, affording 19 g of the quinazolone of the formula

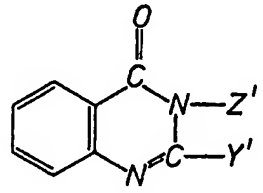
(21)



with a melting point of 215°–219°C. This colour former develops on acid clay a strong greenish yellow shade of excellent fastness to light and sublimation.

The colour formers of the formula

(22)



which are listed in the following table are obtained in the same manner as described in this Example 1.

Table

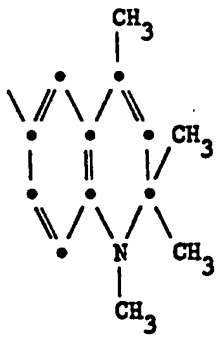
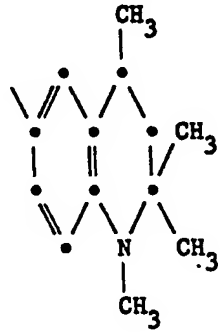
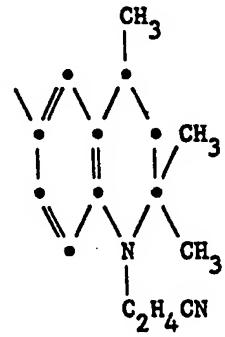
Example No.	Z'	Y'	m.p./°C	Colour
2	H		210-212	greenish yellow
3	H		226-232	greenish yellow
4	H		208-214	greenish yellow

Table (Continution)

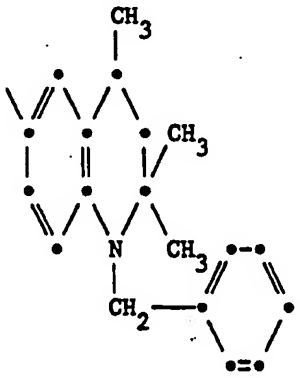
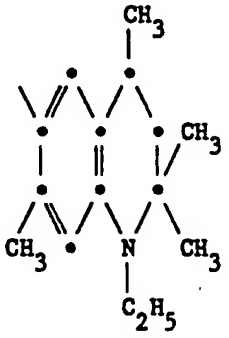
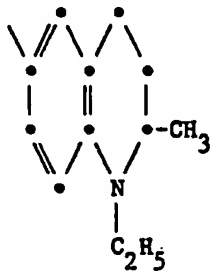
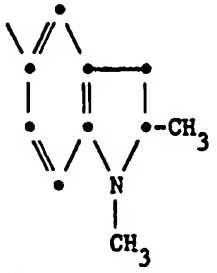
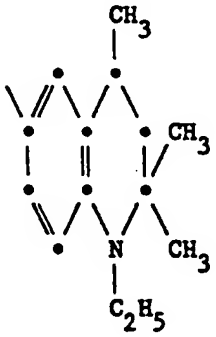
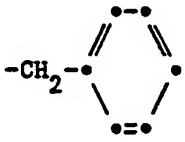
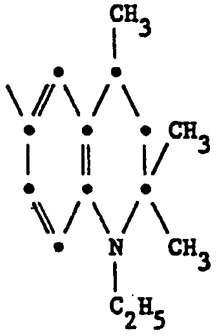
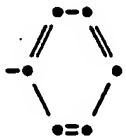
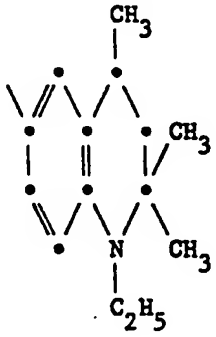
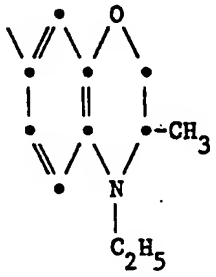
Example No.	z'	Y'	m.p./°C	Colour
5	H		224-230	greenish yellow
6	H		215-216	greenish yellow
7	H		213-216	greenish yellow
8	H		222-226	yellow

Table (Continution)

Example No.	Z'	Y'	m.p./°C	Colour
9	CH_3		resin	greenish yellow
10			171-172	greenish yellow
11			resin	greenish yellow
12	H		216-218	greenish yellow

Example 13: Preparation of a pressure-sensitive copying paper.

A solution of 3 g of the quinazolone of the formula (21) in 80 g of partially hydrogenated terphenyl and 17 g of kerosene and microencapsulated by coacervation in a manner known per se with gelatin and gum arabic. The microcapsules are mixed with starch solution and coated on a sheet of paper. The face of a second sheet of paper is coated with acid-activated bentonite as colour developer. The first sheet and the sheet coated with the developer are laid on top of each other with the coated sides face to face. Pressure is exerted on the first sheet by writing by hand or type-writer and a strong greenish yellow copy of excellent fastness to sublimation and light develops immediately on the sheet coated with the developer.

Corresponding strong yellow copies are fast to sublimation and light are also obtained by using any of the other colour formers of Examples 2 to 12.

Example 14: Following the procedure as described in Example 13, but replacing the quinazolone of the formula (21) by a mixture of the following composition:

1.2 g of 3,3-bis-(4'-dimethylaminophenyl)-6-dimethylaminophthalide,
1.2 g of N-butylcarbazol-3-yl-bis-(4'-N-methyl-N-phenylaminophenyl)-methane,
1.2 g of the quinazolone of the formula (21) and
0.4 g of 3,3-bis-(N-n-octyl-2'-methylindol-3'-yl)phthalide,

there is obtained a pressure-sensitive recording material which gives a strong and lightfast black copy by writing by hand or typewriter.

Example 15: 1 g of the quinazolone of the formula (21) is dissolved in 17 g of toluene. With stirring, 12 g of polyvinyl acetate, 8 g of calcium carbonate and 2 g of titanium dioxide are added to this solution. The resultant suspension is diluted with toluene in the weight ratio 1 : 1 and applied to a sheet of paper with a knife to a thickness of 10 μm. On this sheet of paper is laid a second sheet, the underside of which has been coated to a weight of 3 g/m^2 with a mixture consisting of 1 part of an amide wax, 1 part of a stearin wax and 1 part of zinc chloride. Pressure is exerted on the top sheet by hand or typewriter and a strong greenish yellow copy which is fast to sublimation and light develops immediately on the sheet coated with the colour former.

Example 16: Preparation of a heat-sensitive recording material.

In a ball mill, 32 g of 4,4'-isopropylidenediphenol (bisphenol A), 3.8 g of the distearylamide of ethylenediamine, 39 g of kaolin, 20 g of an 88% hydrolysed polyvinyl alcohol and 500 ml of water are ground to particle size of about 5 μm. In a second ball mill, 6 g of the quinazolone of the formula (21), 3 g of a 88% hydrolysed polyvinyl alcohol and 60 ml of water are ground to particle size of about 3 μm.

Both dispersions are mixed and applied to paper to a dry coating weight of 5.5 g/m^2. A strong greenish yellow colour of excellent fastness to light and sublimation is produced by contacting the paper with a heated ball-point pen.

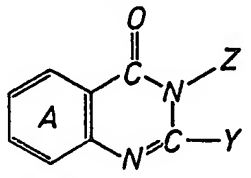
Strong and light fast yellow colours can also be obtained by using any of the other colour formers of Examples 2 to 12.

Example 17: In a ball mill, 2.7 g of the quinazolone of the formula (21), 24 g of N-phenyl-N'-(1-hydroxy-2,2,2-trichloroethyl)-urea, 16 g of stearylamide, 59 g of an 88% hydrolysed polyvinyl alcohol and 58 ml of water are ground to a particle size of 2–5 μm. This suspension is applied to a sheet of paper to a dry coating weight of 5.5 g/m^2. A strong greenish yellow colour which is fast to sublimation and light is obtained by contacting the paper with a ball-point pen.

CLAIMS

1. A chromogenic quinazolone of the formula

(1)



wherein

Y is a polycyclic non-aromatic heterocyclic radical which is attached to the quinazolone moiety through a fused benzene nucleus and is unsubstituted or substituted, and

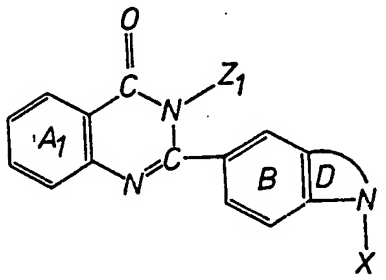
Z is hydrogen, alkyl which contains not more than 12 carbon atoms and is unsubstituted or substituted by halogen, hydroxy, cyano or lower alkoxy, or is cycloalkyl, phenyl, benzyl, or phenyl or benzyl which are each substituted by halogen, nitro, cyano, lower alkyl, lower alkoxy

or lower alkoxycarbonyl, and
the ring A is unsubstituted or substituted by halogen, cyano, nitro, lower alkyl, lower alkoxy or lower alkoxycarbonyl.

2. A quinazolone according to claim 1, wherein Z is hydrogen, lower alkyl, benzyl or phenyl.

3. A quinazolone according to claim 1 or 2, wherein Y is an indolinyl, dihydroquinolinyl, tetrahydroquinolinyl or benzomorpholino radical.

4. A quinazolone according to claim 1, of the formula

(2) 

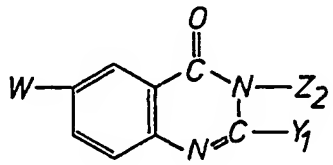
wherein
X is hydrogen, alkyl which contains not more than 8 carbon atoms and is unsubstituted or substituted by halogen, cyano or lower alkoxy, or is cycloalkyl or benzyl,
Z_1 is alkyl which contains not more than 8 carbon atoms and is unsubstituted or substituted by lower alkoxy, or is cyclohexyl, phenyl, naphthyl, benzyl, or phenyl or benzyl which are substituted by halogen, cyano, lower alkyl, lower alkoxy or lower alkoxycarbonyl, and the rings
A_1 and B, each independently of the other, are unsubstituted or substituted by cyano, halogen, lower alkyl, or lower alkoxy, and the ring
B is a hydrogenated 5- or 6-membered N-heterocyclic ring which is unsubstituted or C-substituted by one or more of the same or different substituents selected from halogen, cyano, hydroxyl, lower alkyl, lower alkoxy, C_5–C_6cycloalkyl, benzyl and C_3–C_6alkylene.

5. A quinazolone according to claim 4, wherein Z_1 is hydrogen, lower alkyl, benzyl or phenyl.

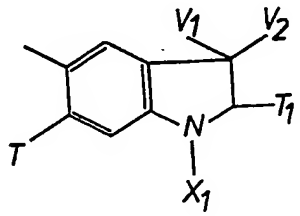
6. A quinazolone according to claim 4 or 5, wherein the ring D is 6-membered and C-substituted by 1, 2 or 3 methyl groups.

7. A quinazolone according to any one of claims 4 to 6, wherein X is lower alkyl, benzyl or β-cyanoethyl.

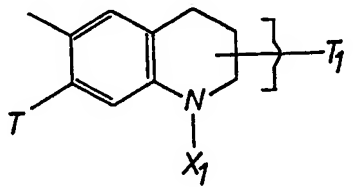
8. A quinazolone according to claim 1, of the formula

(3) 

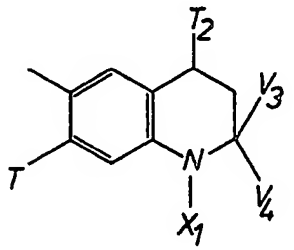
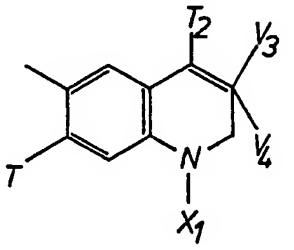
wherein
Z_2 is hydrogen, lower alkyl, phenyl or benzyl,
W is hydrogen, halogen, methyl or methoxy, and
Y_1 is a 5-indolinyl radical of the formula

(3a) 

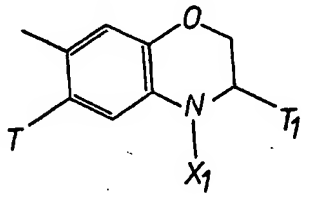
a tetrahydroquinolinyl radical of the formula

(3b) 

a hydrogenated quinoline radical of the formula

(3c)  or  (3d)

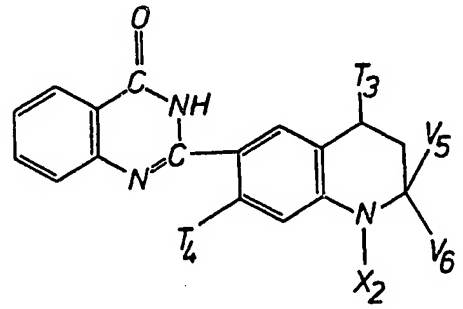
or a benzomorpholino radical of the formula

(3e) 

X_1 is hydrogen, C_1–C_8alkyl, C_2–C_6alkoxyalkyl, β-cyanoethyl or benzyl,
T is hydrogen, halogen, lower alkyl, lower alkoxy, C_1–C_4acylamino or phenyl,
T_1 and T_2 are each hydrogen, halogen, hydroxy, lower alkyl or lower alkoxy, and
V_1, V_2, V_3 and V_4 are each hydrogen, lower alkyl, cycloalkyl or benzyl, or (V_1 and V_2) or (V_3 and V_4) are each together alkylene.

9. A quinazolone according to claim 8, wherein Y_1 is the tetrahydroquinoline radical of the formula (3c).

10. A quinoazolone according to claim 9, of the formula

(4) 

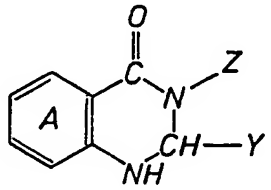
wherein
X_2 is C_1–C_8alkyl, β-cyanoethyl or benzyl,
T_3, V_5 and V_6 are each lower alkyl, and
T_4 is hydrogen or methyl.

11. A quinazolone according to claim 8, wherein Y_1 is the tetrahydroquinolinyl radical of the formula (3b).

12. A quinazolone according to claim 8, wherein Y_1 is the benzomorpholino radical of the formula (3e).

13. A quinazolone according to claim 8, wherein Y_1 is the 5-indolinyl radical of the formula (3a).

14. A process for the manufacture of the quinazolones of the formula as defined in claim 1, which process comprising oxidising a 1,2,3,4-tetrahydroquinazol-4-one of the formula

(5) 

wherein A, Z and Y have the meanings given in claim 1.

15. A pressure-sensitive or heat-sensitive recording material which comprises a support which contains, or has coated thereon as colour former, at least one quinazolone of the formula as defined in any one of claims 1 to 13.

16. The pressure-sensitive recording material of claim 15, wherein the quinazolone is dissolved in an organic solvent, and which recording material further comprises at least one solid electron acceptor.

17. The pressure-sensitive recording material of claim 16, wherein the quinazolone is encapsulated in microcapsules.

18. The pressure-sensitive recording material of claim 17, wherein the encapsulated quinazolone is present in the form of a layer on the back of a transfer sheet and the electron acceptor is present in the form of a layer on the face of a receiving sheet.

19. The pressure-sensitive recording material of claim 15, which comprises the quinazolone together with one or more other colour formers.

20. The heat-sensitive recording material of claim 15, which comprises in at least one layer, at least one quinazolone colour former, at least one electron acceptor and at least one binder.

21. A quinazolone according to claim 1 substantially as hereinbefore described with reference to any one of Examples 1 to 12.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1985, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.